

TITLE

ORGANICALLY FUNCTIONALIZED CARBON NANOCAPSULE

BACKGROUND OF THE INVENTION

Field of the invention

5 The present invention relates to carbon nanocapsules, and more particularly to functionalized carbon nanocapsules.

Description of the Related Art

10 A carbon nanocapsule is a polyhedral carbon cluster constituted by multiple graphite layers having a balls-within-a ball structure. The diameter of a carbon nanocapsule is about 3-100 nm. There are two types of carbon nanocapsules: hollow and metal-filled. The center of a hollow carbon nanocapsule is, of course, hollow,
15 while that of a metal-filled nanocapsule is filled with metals, metal oxides, metal carbides, or alloys.

 Carbon nanocapsules were first discovered with carbon nanotubes in 1991, in the process of producing carbon nanotubes. Owing to the strong van der Waals
20 force between carbon nanocapsules and carbon nanotubes, it is not easy to isolate carbon nanocapsules from the carbon nanotubes. In addition, the amount of carbon nanocapsules produced with carbon nanotubes is only enough for structural observation under electron
25 microscope, thus the application thereof is obstructed.

 By continuous research, processes producing high-purity hollow carbon nanocapsules as well as magnetic metal-filled carbon nanocapsules have been developed.

(Please refer to US patent application No. _____ and _____) With their special fullerene structure and optoelectronic properties, carbon nanocapsules can be utilized in various fields such as medicine (medical grade active carbon), light and heat absorption, electromagnetic shielding, organic light emitting materials, solar energy receivers, catalysts, sensors, carbon electrodes in lithium batteries, nanoscale composite materials with thermal conductivity and special electrical properties, and nanoscale carbon powder for printing. However, owing to the non-solubility of carbon nanocapsules, the related application is limited and insufficient.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to functionalize the carbon nanocapsules to prepare organically-functionalized carbon nanocapsules, thereby expanding the application thereof.

Therefore, the invention provides an organically-functionalized carbon nanocapsule. The organically-functionalized carbon nanocapsule includes a carbon nanocapsule and at least one kind of organic functional groups bonded thereon. The organically-functionalized carbon nanocapsule is of the following formula: $F(-E)_n$, in which F is the carbon nanocapsule, E is the organic functional group, and n is the number of the organic functional group.

According to the invention, the carbon nanocapsule is a polyhedral carbon cluster constituting multiple

graphite layers having a balls-within-a ball structure, and the diameter of a carbon nanocapsule is 3-100 nm.

According to the invention, the carbon nanocapsule is a hollow carbon nanocapsule or a metal-filled carbon nanocapsule filled with metals, metal oxides, metal carbides, or alloys.

Before preparing organically-functionalized carbon nanocapsules, high-purity carbon nanocapsules must be prepared first, by the preparation method described, for example, in the above-mentioned references. The carbon nanocapsule obtained is a polyhedral carbon cluster constituting multiple graphite layers having a balls-within-a ball structure, wherein the diameter of a carbon nanocapsule is 3-100 nm. The carbon nanocapsules for preparation of organically-functionalized carbon nanocapsules can be hollow or filled with metals, metal oxides, metal carbides, or alloys.

By functionalization of the carbon nanocapsule, at least one kind of functional group is bonded on the carbon nanocapsule, thereby increasing its reactivity. By functionalization with different functional groups, the reactive variety thereof is enriched, and thereby the application is expanded.

The functionalizing methods of carbon nanocapsules applied in the invention are analogic to those of carbon 60. However, owing to the relatively greater size of carbon nanocapsules, the nano-dispersing technique is important for the control of chemical modifying effects. In addition, carbon nanocapsules have different optical, electrical, and magnetic properties from carbon nanotubes

and carbon 60, thus the organically-functionalized carbon nanocapsules have distinct applications.

The carbon nanocapsules can be functionalized by a redox reaction, cycloaddition reaction, or a radical addition reaction.

In the redox reaction, the carbon nanocapsule is reacted with a strong oxidant, for example, $\text{H}_2\text{SO}_4 + \text{HNO}_3$, OSO_4 , KMnO_4 or O_3 , to oxidize the surface carbon layer of the carbon nanocapsule and form a functional group, for example, $-\text{OH}$, $-\text{C}=\text{O}$, $-\text{CHO}$ or $-\text{COOH}$, on the carbon nanocapsule.

In the cycloaddition reaction, the carbon nanocapsule is functionalized via the double bonds on the surface of the carbon nanocapsule. Compounds such as aniline, N,N -dimethylaniline, CH_2O (aldehyde), $\text{CH}_3\text{NHCH}_2\text{COOH}$ (N -substituted glycine derivative), or $(\text{CHCl}_3 + \text{KOH})$, are reacted with the carbon nanocapsule to form functional groups, for example, $-\text{NHAr}$, $-\text{N}^+(\text{CH}_3)_2\text{Ar}$, $=\text{CCl}_2$ or amino groups, on the carbon nanocapsule.

In the radical addition reaction, the carbon nanocapsule is functionalized via the double bonds on the surface of the carbon nanocapsule. The carbon nanocapsule is reacted with a free-radical initiator or molecules capable of producing radicals, for example, $\text{K}_2\text{S}_2\text{O}_8$, H_2O_2 , methylmethacrylate, or azobisisobutyronitrile (AIBN), to bond functional groups, for example, $-\text{OSO}_3^-$, $-\text{OH}$, $-\text{C}(\text{CH}_3)_2\text{COOCH}_3$ or $-\text{C}(\text{CH}_3)_2\text{CN}$ on the carbon nanocapsule.

In the above three kinds of preparation methods, the method involving redox reaction is quite different from

the conventional preparation methods of fullerene derivatives. In the redox reaction, strong oxidants are applied to oxidize the surface layers of carbon nanocapsules to form functional groups, for example, -OH, -C=O, -CHO or -COOH, on the surface of carbon nanocapsules. The functionalized carbon nanocapsules are then able to react with any other compounds to form more complicated functionalized carbon nanocapsules. In the preparation methods of fullerene derivatives, however, oxidants are not applied because of the different structure of fullerene molecules. Strong oxidants functionalize molecules by breaking bonds between carbon atoms, which cause damage to a fullerene structure, while still applicable on a carbon nanocapsule by virtue of the multiple-graphite-layer structure.

In addition, U.S. Patent No. 5,177,248 and U.S. Patent No. 5,294,732 incorporated herein by reference describe other preparation methods of organically-functionalized carbon nanocapsules.

By functionalization of carbon nanocapsule, an organically-functionalized carbon nanocapsule is provided, comprising a carbon nanocapsule and at least one kind of organic functional group bonded thereon, wherein the organically-functionalized carbon nanocapsule is of the following formula: $F(-E)_n$, in which F is the carbon nanocapsule, E is the organic functional group, and n is the number of the organic functional group. The preferable range of n is 1-100,000.

In the organically-functionalized carbon nanocapsule, each E is independently E₁, E₂, E₃, E₄ or E₅, in which each E₁, independently, is Y₁,Y₂ -amino, (Y₁,Y₂ -alkyl)amino, Y₁,Y₂ -ethylenediamino, (dihydroxymethyl)alkylamino, (X₁,X₃ -aryl)amino, or X₁,X₃ -aryloxy; each E₂, independently, is Y₁,Y₂ -alkoxy, (Y₁,Y₂ -amino)alkoxy, (Y₁,Y₂,Y₃ -aryl)oxy, (dihydroxyalkyl)aryloxy, (Y₁,Y₂,Y₃ -alkyl)amino, (Y₁,Y₂,Y₃ -aryl)amino, or dihydroxyalkylamino; each E₃, independently, is Y₁,Y₂,Y₃ -alkoxy, (trihydroxyalkyl)alkoxy, (trihydroxyalkyl)alkylamino, (dicarboxyalkyl)amino, (Y₁,Y₂,Y₃ -alkyl)thio, (X₁,X₂ -aryl)thio, (Y₁,Y₂ -alkyl)thio, (dihydroxyalkyl)thio, Y₁,Y₂ -dioxoalkyl; each E₄, independently, is ((glycosidyl)oxoheteroaryl)amino, ((glycosidyl)oxoaryl)amino, (X₁,X₂,X₃ -heteroaryl)amino, (X₁ -diarylketone)amino, (X,X₁ -oxoaryl)amino, (X,X₁ -dioxoaryl) amino, (Y₁ -alkyl, Y₂ -alkyldioxoheteroaryl)amino, (Y₁ -alkyl, Y₂ -alkyldioxoaryl)amino, (di(Y₁,Y₂ -methyl)dioxoheteroaryl)amino, (di(Y₁,Y₂ -methyl)dioxoaryl)amino, ((glycosidyl)heteroaryl)amino, ((glycosidyl)aryl)amino, ((carboxylacetylalkyl)oxoheteroaryl)amino, ((carboxylacetylalkyl)oxoaryl)amino, ((isopropylaminohydroxyalkoxy)aryl)amino, or (X₁,X₂,X₃ -alkylaryl)amino; each E₅, independently, is (X₁,X₂,X₃ -heteroaryl)oxy, (isopropylaminohydroxyalkyl)aryloxy, (X₁,X₂,X₃ -oxoheteroaryl)oxy, (X₁,X₂,X₃ -oxoaryl)oxy, (X₁,Y₁ -oxoheteroaryl)oxy, (X₁ -diarylketone)oxy, (X,X₁ -oxoaryl)oxy, (X₁,X₂ -dioxoaryl)oxy, (Y₁,Y₂,di-

aminodihydroxy) alkyl, (X₁, X₂ -heteroaryl) thio,
((tricarboxylalkyl) ethylenediamino) alkoxy, (X₁, X₂ -
oxoaryl) thio, (X₁, X₂ -dioxoaryl) thio,
(glycosidylheteroaryl) thio, (glycosidylaryl) thio, Y₁ -
5 alkyl(thiocarbonyl) thio, Y₁, Y₂ -alkyl(thiocarbonyl) thio,
Y₁, Y₂, Y₃ -alkyl(thiocarbonyl) thio, (Y₁, Y₂ -
aminothiocarbonyl) thio, (pyranosyl) thio, cysteinyl,
tyrosinyl, (phenylalanyl) amino, (dicarboxyalkyl) thio,
(aminoaryl)₁₋₂₀ amino, or (pyranosyl) amino;

10 each X, independently, is halide; each of X₁ and X₂,
independently, is --H, --Y₁, --O--Y₁, --S--Y₁, --NH--Y₁, --
CO--O--Y₁, --O--CO--Y₁, --CO--NH--Y₁, --CO--NY₁Y₂, --NH--
CO--Y₁, --SO₂--Y₁, --CHY₁Y₂, or --NY₁Y₂ ; each X₃,
independently, is --Y₁, --O--Y₁, --S--Y₁, --NH--Y₁, --CO--
15 O--Y₁, --O--CO--Y₁, --CO--NH--Y₁, --CO--NY₁Y₂, --NH--CO--
Y₁, --SO₂--Y₁, --CHY₁Y₂ or --NY₁Y₂;

each of Y₁, Y₂ and Y₃, independently, is --B--Z;

each B, independently, is --R_a--O--[Si(CH₃)₂--O--]<sub>1-
100</sub>, C₁₋₂₀₀₀ alkyl, C₆₋₄₀ aryl, C₇₋₆₀ alkylaryl, C₇₋₆₀ arylalkyl,
20 (C₁₋₃₀ alkyl ether)₁₋₁₀₀, (C₆₋₄₀ aryl ether)₁₋₁₀₀, (C₇₋₆₀
alkylaryl ether)₁₋₁₀₀, (C₇₋₆₀ arylalkyl ether)₁₋₁₀₀, (C₁₋₃₀
alkyl thioether)₁₋₁₀₀ (C₆₋₄₀ aryl thioether)₁₋₁₀₀, (C₇₋₆₀
alkylaryl thioether)₁₋₁₀₀, (C₇₋₆₀ arylalkyl thioether)₁₋₁₀₀,
(C₂₋₅₀ alkyl ester)₁₋₁₀₀, (C₇₋₆₀ aryl ester)₁₋₁₀₀, (C₈₋₇₀
25 alkylaryl ester)₁₋₁₀₀, (C₈₋₇₀ arylalkyl ester)₁₋₁₀₀, --R--CO--
O--(C₁₋₃₀ alkyl ether)₁₋₁₀₀, --R--CO--O--(C₆₋₄₀ aryl ether)<sub>1-
100</sub>, --R--CO--O--(C₇₋₆₀ alkylaryl ether)₁₋₁₀₀, --R--CO--O--
(C₇₋₆₀ arylalkyl ether)₁₋₁₀₀, (C₄₋₅₀ alkyl urethane)₁₋₁₀₀ (C₁₄₋₆₀

aryl urethane)₁₋₁₀₀, (C₁₀₋₈₀ alkylaryl urethane)₁₋₁₀₀ (C₁₀₋₈₀
arylalkyl urethane)₁₋₁₀₀, (C₅₋₅₀ alkyl urea)₁₋₁₀₀, (C₁₄₋₆₀ aryl
urea)₁₋₁₀₀ (C₁₀₋₈₀ alkylaryl urea)₁₋₁₀₀, (C₁₀₋₈₀ arylalkyl urea)
1-100, (C₂₋₅₀ alkyl amide)₁₋₁₀₀, (C₇₋₆₀ aryl amide)₁₋₁₀₀, (C₈₋₇₀
5 alkylaryl amide)₁₋₁₀₀ (C₈₋₇₀ arylalkyl amide)₁₋₁₀₀, (C₃₋₃₀
alkyl anhydride)₁₋₁₀₀, (C₈₋₅₀ aryl anhydride)₁₋₁₀₀, (C₉₋₆₀
alkylaryl anhydride)₁₋₁₀₀, (C₉₋₆₀ arylalkyl anhydride)₁₋₁₀₀,
(C₂₋₃₀ alkyl carbonate)₁₋₁₀₀, (C₇₋₅₀ aryl carbonate)₁₋₁₀₀, (C₈₋₆₀
alkylaryl carbonate)₁₋₁₀₀, (C₈₋₆₀ arylalkyl carbonate)₁₋₁₀₀, -
10 -R₁--O--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--(C₁₋₃₀ alkyl
ether, C₆₋₄₀ aryl ether, C₇₋₆₀ alkylaryl ether, or C₇₋₆₀
arylalkyl ether)₁₋₁₀₀, --R₁--O--CO--NH--(R₂ or Ar--R₂--Ar)-
-NH--CO--O(C₂₋₅₀ alkyl ester, C₇₋₆₀ aryl ester, C₈₋₇₀
alkylaryl ester, or C₈₋₇₀ arylalkyl ester)₁₋₁₀₀, --R₁--C--CO-
15 -NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--(C₁₋₃₀ alkyl ether, C₆₋₄₀
aryl ether, C₇₋₆₀ alkylaryl ether, or C₇₋₆₀ arylalkyl
ether)₁₋₁₀₀, --CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--, --R₁
--O--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--(C₂₋₅₀ alkyl
ester, C₇₋₆₀ aryl ester, C₈₋₇₀ alkylaryl ester, or C₈₋₇₀
20 arylalkyl ester)₁₋₁₀₀, --R₃--O--CO--NH--(R₂ or Ar--R₂--Ar)--
NH--CO--O--, --R₁--NH--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO-
-O--(C₁₋₃₀ alkyl ether, C₆₋₄₀ aryl ether, C₇₋₆₀ alkylaryl
ether, or C₇₋₆₀ arylalkyl ether)₁₋₁₀₀, --R₁--NH--CO--NH--(R₂
or Ar--R₂--Ar)--NH--CO--O--(C₂₋₅₀ alkyl ester, C₇₋₆₀ aryl
25 ester, C₈₋₇₀ alkylaryl ester, or C₈₋₇₀ arylalkyl ester)₁₋₁₀₀,
--R₁--NH--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--(C₁₋₃₀
alkyl ether, C₆₋₄₀ aryl ether, C₇₋₆₀ alkylaryl ether, or C₇₋₆₀
arylalkyl ether)₁₋₁₀₀, --CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO-
-O--, --R₁--NH--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--(C₂₋
30 ₅₀ alkyl ester, C₇₋₆₀ aryl ester, C₈₋₇₀ alkylaryl ester, or

C₈₋₇₀ arylalkyl ester)₁₋₁₀₀, --R₃--O--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--O--, --R₁--O--CO--NH--(R₂ or Ar--R₂--Ar)--NH--CO--NH--(C₂₋₅₀ alkyl amide, C₇₋₆₀ aryl amide, C₈₋₇₀ alkylaryl amide, or C₈₋₇₀ arylalkyl amide)₁₋₁₀₀, or --R₁--NH--CO--NH--(R₂ or Ar--R₂--Ar)NH--CO--NH--(C₂₋₅₀ alkyl amide, C₇₋₆₀ aryl amide, C₈₋₇₀ alkylaryl amide, or C₈₋₇₀ arylalkyl amide)₁₋₁₀₀;

each Z, independently, is --C--D--, wherein each C, independently, is --R--, --R--Ar--, --Ar--R--, or --Ar--; and each D, independently, is --OH, --SH, --NH₂, --NHOH, --SO₃H, --OSO₃H, --COOH, --CONH₂, --CO--NH--NH₂, --CH(NH₂)--COOH, --P(OH)₃, --PO(OH)₂, --O--PO(OH)₂, --O--PO(OH)--O--PO(OH)₂, --O--PO(O⁻)--O--CH₂CH₂NH₃⁺, -glycoside, --OCH₃, --O--CH₂--(CHOH)₄--CH₂₄--CH, --O--CH₂--(CHOH)₂--CHOH, --C₆H₃(OH)₂, --NH₃⁺, --N⁺HR_bR_c, or N⁺HR_bR_cR_d; wherein each of R, R₁, R₂, R₃, R_a, R_b, R_c, and R_d independently, is C₁₋₃₀ alkyl, each Ar, independently, is aryl.

DESCRIPTION OF THE DRAWINGS

The present invention can be more fully understood by reading the subsequent detailed description and examples with references made to the accompanying drawings, wherein:

FIG. 1 illustrates the functionalization of carbon nanocapsules involving a redox reaction;

FIG. 2a illustrates the functionalization of carbon nanocapsules involving a cycloaddition reaction in the example 2a; and

FIG. 2b illustrates the functionalization of carbon nanocapsules involving a radical addition reaction in the example 2b.

DETAILED DESCRIPTION OF THE INVENTION

Example 1

Redox reaction

FIG. 1 illustrates the functionalization of carbon nanocapsules involving a redox reaction.

A reaction flask (1L) was charged with carbon nanocapsules (1.0g) dissolved in sulfuric acid/nitric acid (weight ratio=1:1). The mixture was stirred by an ultrasonic cleaner for 10 mins, and then heated to about 140°C and refluxed for 2 hours. Afterwards, the mixture was centrifuged to separate the carbon nanocapsules from the strong acid, rinsing the carbon nanocapsules thoroughly followed by several centrifuges, until the pH value of carbon nanocapsules approached 7. The carbon nanocapsules obtained were black with -COOH groups bonded thereon. By titration using NaOH, the concentration of the -COOH groups was identified as 13 μ moles/ per gram carbon nanocapsules. The oxidization of carbon nanocapsules resulted in damage of the surface carbon layers, which could be observed under a transmission electron microscope. The organically-functionalized carbon nanocapsules were soluble in water by virtue of the -COOH groups.

Example 2

Cycloaddition reaction

Example 2a

FIG. 2a illustrates the functionalization of carbon nanocapsules involving a cycloaddition reaction in the example 2a.

A reaction flask (1L) was charged with carbon nanocapsules (1.0g) dissolved in a saturated DMF(dimethyl formamide) solution of aldehyde and N-substituted glycine derivative (molar ratio=1:1). The mixture was then stirred by an untrasonic cleaner for 10 mins, and heated to about 130°C and refluxed for 120 hours. Afterwards, the mixture was centrifuged to separate the carbon nanocapsules from the solution. The reaction was as shown in FIG. 2a, with a product soluble in chloroform or water.

example 2b

FIG. 2b illustrates the functionalization of carbon nanocapsules involving a radical addition reaction in the example 2b.

A reaction flask (1L) was charged with carbon nanocapsules (1.0g) dissolved in N,N-dimethylaniline (500ml). The mixture was then stirred by an untrasonic cleaner for 10 mins, heated, and refluxed for 12 hours. Afterwards, the mixture was centrifuged to separate the carbon nanocapsules from the solution. The reaction was as shown in FIG. 2b, with a product soluble in water.

Example 3

Radical addition reaction

Example 3a

A reaction flask (1L) was charged with carbon nanocapsules (100 mg) and $K_2S_2O_8$ (120 mg) dissolved in water (500ml). The solution mixture was purged with N_2 prior to stirring and heating to $70^\circ C$ for 5 hours. The product was black carbon nanocapsules with $-OSO_3^-$ groups bonded thereon, easily soluble in water. The radical addition reaction was observed by the electron spin resonance spectrum (ESR), in which the signal at $g=2.0032$, $\Delta H_{pp}=4.32G$ represents the bonding of radicals.

example 3b

A reaction flask (1L) was charged with carbon nanocapsules (100 mg) and methylmethacrylate (25 ml) dissolved in toluene (250ml). The solution mixture was illuminated at room temperature to initiate radical generation of methylmethacrylate, thereby reacting with the surface double bonds of the carbon nanocapsules. The radical addition reaction was observed by the electron spin resonance spectrum (ESR), in which signals at $g=2.0033$, $\Delta H_{pp}=8.56G$ and $g=2.0037$, $\Delta H_{pp}=4.44G$ represent the bonding of radicals.

The foregoing description has been presented for purposes of illustration and description. Obvious modifications or variations are possible in light of the above teaching. The embodiments were chosen and described to provide the best illustration of the principles of this invention and its practical

application to thereby enable those skilled in the art to
utilize the invention in various embodiments and with
various modifications as are suited to the particular use
contemplated. All such modifications and variations are
5 within the scope of the present invention as determined
by the appended claims when interpreted in accordance
with the breadth to which they are fairly, legally, and
equitably entitled.